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13. ABSTRACT (Maximum 200 words)

This report extends from our report of July 12, 1993 to completion. We focused our efforts on laboratory and field studies of easy release and antifouling coatings and their additives. Goals were: 1.) understanding how the best coatings prevent barnacle fouling; and 2.) developing the ability to predict when, and to determine why, coatings fail. Leaching of additives from foul release coatings plays a significant role in prevention of larval settlement on all of the best antifouling and foul release coatings. Some additives are broad spectrum toxicants, while others are toxic to specific kinds of larvae by altering their immediate environment. All effective coatings produced leachates toxic to barnacle larvae. Measuring additive levels in coatings and the rate of leaching from experimental coatings into water can be used to predict when coatings will fail. In collaboration with scientists at the University of New Hampshire, we showed the utility of experimental approaches in which coatings were designed to fail predictably over time. In addition to this work, we met our responsibilities in the area of patents and publications.

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Rittschof, Gerhart, Clare

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This report extends from our last report of July 12, 1993 to the present. During this interval, we focused our efforts on laboratory and field studies of easy release and antifouling coatings and their additives. The goals of these studies were twofold: 1. understanding how the best coatings prevent barnacle fouling; 2. developing the ability to predict when and determine why coatings fail.

We showed and concluded that leaching additives play a significant role in prevention of larval settlement on all of the best antifouling and foul release coatings. Some agents are broad spectrum toxicants while others may be toxic to specific kinds of larvae by altering their immediate environment. All effective coatings produced leachates toxic to barnacle larvae. Measuring additive levels in coatings and the rate of leaching from experimental coatings into water can be used to predict when coatings will fail due to additive depletion. We developed, based upon type of fouling organisms, cluster analysis approaches that show that all effective coatings grow together with toxic coatings. In collaboration with scientists at the University of New Hampshire, we showed the utility of experimental approaches in which coatings were designed to fail precitably. In addition to this work which was reported at the meetings we have met our responsibilities in the area of patents and publications. These are reported below.

We continued efforts on the patenting of technologies developed by the Duke antifouling program. The following is the status of the Duke technologies.

PATENTING AND TECHNOLOGY TRANSFER -- DUKE UNIVERSITY PROGRAM

PATENTS ISSUED:

Costlow, J.D., Hooper, I.R., and Rittschof, D. *Anti-fouling compound and method of use.* U.S. Patent #4,788,302 awarded on November 29, 1988. (General subject area: antifouling agents from the octocorals *Leptogorgia virgulata* and *Renilla reniformis*). We are not actively pursuing this technology because it is less commercially feasible than our other related technologies.

Gerhart, D.J., Rittschof, D., and Hooper, I.R. *Antifouling composition comprising lactone compounds, methods for protecting aquatic structures, and articles protected against fouling organisms.* U.S. Patent # 5,248,221 awarded September 28, 1993. Intent to file foreign patents identified (PCT Application filed 13 October 1993). (General subject area: lactone analogs of natural antifoulants)

Gerhart, D.J., Rittschof, D., and Bonaventura, J. *Antifouling coating comprising steroidal compounds and method for using same.* U.S. Patent #5,252,630 awarded on October 12, 1993. (General subject area: steroidal toxins for fouling control)

Gerhart, D.J., Rittschof, D., Hooper, I.R., and Clare, A.S. *Antifouling composition comprising furan compounds, methods for protecting aquatic structures, and articles protected against fouling organisms.* U.S. Patent # 5,259,701 awarded November 9, 1993. Intent to file foreign patents identified (PCT Application filed 13 October 1993). (General subject area: furan analogs of natural antifoulants)

Gerhart, D.J., Rittschof, D., and Bonaventura, J. *Antifouling coating and method for using same.* U.S. Patent # 5,314,932 awarded May 24, 1994. [Duke File No. 00562 DIV.]

Gerhart, D.J. *Antifouling coating comprising cyclohexane compounds and method for using same.* Filed October 15, 1992 with the United States Patent and Trademark Office. In review by the USPTO. (General subject area: cyclohexane analogs of natural antifoulants)

TRANSITION TO INDUSTRY: STATUS OF DUKE-DEVELOPED TECHNOLOGIES:

An option to license the furan, lactone, and cyclohexene analogs is currently held by Rohm & Haas Company. Industrial application is being examined by this corporation.

Licensees are being sought for the steroidal antifoulant molecules. Industrial application is complicated by the toxic nature of these substances. However, specific industries have indicated an interest.

Technologies identified in the Costlow et al. patent (U.S. patent #4,788,302) are not under license. Licensees are not being sought. Potential industrial application is unlikely at this time due to the limited availability of the natural compounds or extracts containing them, and the expense associated with synthesizing and purifying active compounds.

Scholarly Contributions Resulting from ONR Funding

PUBLICATIONS IN PRESS

Bryan, P.J., D. Rittschof, and J.B. McClintock. Bioactivity of echinoderm ethanolic body-wall extracts: An assessment of marine bacterial attachment and macroinvertebrate larval settlement. *J. exp. Mar. Biol. Ecol.*

Clare, A.S., D. Rittschof, R.R. Price, and D.J. Gerhart. Khellin, a natural product analogue with antifouling activity: Laboratory and field studies. In *Proc. 9th International Biodeterioration and Biodegradation Symposium,* Leeds, August 1993.

Clare, A.S., R.F. Thomas, and D. Rittschof. Evidence for the involvement of cyclic AMP in the pheromonal modulation of barnacle settlement. *J. exp. Biol.*

Maki, J., M.-O. Samuelsson, D. Rittschof, U. Szewzyk, S. Kjelleberg and R. Misahevl. Substratum/bacterial interactions and their effect on the attachment of *Balanus amphitrite* cypris larvae. *Microb. Ecol.*

Sasikumar, N., A.S. Clare, D.J. Gerhart, D. Stover, and D. Rittschof. Comparative toxicities of selected compounds to nauplii of *Balanus amphitrite amphitrite* Darwin and *Artemia* sp. *Bull. Environ. Contam. Toxicol.*

Vasishtha, N., D.C. Sundberg, and D. Rittschof. Evaluation of release rates and control of biofouling using monolithic coatings containing an isothiazolone. *Biofouling.*

PUBLICATIONS OF THE LAST FOUR (4) YEARS

Clare, A.S., S.C. Ward, D. Rittschof, and K.M. Wilbur. **1994.** Growth increments of the bartnacle *Balanus amphitrite amphitrite* Darwin (Cirripedia). *J. Crustacean Biol.* 14(1):27-35.

Maki, J., A.B. Yule, D. Rittschof, and R. Mitchell. **1994.** The effect of bacterial films on the temporary adhesion and permanent fixation of cypris larvae, *Balanus amphitrite* Darwin. *Biofouling* 8:121-131.

Price, R.R., M. Patchan, D. Rittschof, A.S. Clare, and J. Bonaventura. **1994.** Performance enhancement of natural antifouling compounds and their analogs through microencapsulation and controlled release. In: *Recent Developments in Biofouling Control,* M.-F. Thompson, R. Nagabhushanam, R. Sarojini, and M. Finerman (eds.), pp. 321-334. Oxford and IBH Publ. Co., New Delhi.

Rittschof, D., N. Sasikumar, D. Murlless, A.S. Clare, D.J. Gerhart, and J. Bonaventura. **1994.** Mixture interactions of lactones, furans, and a commercial biocide: toxicity and antibarnacle settlement activity. In: *Recent Developments in Biofouling Control,* M.-F. Thompson, R. Nagabhushanam, R. Sarojini, and M. Fingerman (eds.), pp. 269-274. Oxford and IBH Publ. Co., New Delhi.

Katz, J.N. and D. Rittschof. **1993.** Alarm/investigation responses of hermit crabs as related to shell fit and crab size. *Mar. Behav. Physiol.* 22:171-182.

Pechenik, J.A., D. Rittschof, and A.R. Schmidt. **1993.** Influence of delayed metamorphosis on survival and growth of juvenile barnacles *Balanus amphitrite. Mar. Biol.* 115:287-294.

Rittschof, D. **1993.** Body odors and neutral-basic peptide mimics: A review of responses by marine organisms. *Am. Zool.* 33:487-493.

Sr. Avelin Mary, Sr. Vitalina Mary, D. Rittschof, and R. Nagabhushanam. **1993.** Bacterial/barnacle interaction: The potential of using juncellins and antibiotics to alter structure of bacterial communities. *J. Chem. Ecol.* 19(10):2155-2167.

Clare, A.S., D. Rittschof, and J.D. Costlow, Jr. **1992.** Effects of the nonsteroidal ecdysone mimic RH 5849 on larval crustaceans. *J. Exp. Zool.* 262:436-440.

Clare, A.S., D. Rittschof, D.J. Gerhart and J.S. Maki. **1992.** Molecular approaches to non-toxic antifouling. *Invert. Reprod. Dev.* 22:67-77.

Gerhart, D.J., D. Rittschof, I.R. Hooper, K. Eisenman, A.E. Meyer, R.E. Baier, and C. Young. **1992.** Rapid and inexpensive quantification of the combined polar components of surface wettability: Application to biofouling. *Biofouling* 5:251-259.

Holström, C., D. Rittschof, and S. Kjelleberg. **1992.** Inhibition of settlement by larvae of *Balanus amphitrite* and *Ciona intestinalis* by a surface-colonizing marine bacterium. *Appl. Environ. Microbiol.* 58(7):2111-2115.

Maki, J.S., D. Rittschof, and R. Mitchell. **1992.** Inhibition of larval barnacle attachment to bacterial films: An investigation of physical properties. *Microb. Ecol.* 23:97-106.

Price, R., M. Patchan, D. Rittschof, A. Clare, and J. Bonaventura. **1992.** Elimination of rosin from vinyl antifouling coatings by the use of novel cylindrical channel forming microtubules. *Transactions of Institute of Marine Sciences.*

Price, R.R., M. Patchan, D. Rittschof, A.S. Clare, and J. Bonaventura. **1992.** Performance enhancement of natural antifouling compounds and their analogs through microencapsulation and controlled release. *Biofouling* 6:207-216.

Rittschof, D., A.S. Clare, D.J. Gerhart, Sister Avelin Mary, and J. Bonaventura. **1992.** Barnacle *in vitro* assays for biologically active substances: toxicity and settlement assays using mass cultured *Balanus amphitrite amphitrite* Darwin. *Biofouling* 6:115-122.

Rittschof, D., A.S. Clare, D.J. Gerhart, J. Bonaventura, C. Smith, and M. Hadfield. **1992.** Rapid field assessment of antifouling and foul-release coatings. *Biofouling* 6:181-192.

Walker, G., A.S. Clare, D. Rittschof, and D. Mensching. **1992.** Aspects of the life-cycle of *Loxothylacus panopaei* (Gissler), a sacculinid parasite of the mud crab, *Rhithropanopeus harrisii* (Gould): A laboratory study. *J. exp. Mar. Biol. Ecol.* 157:181-193.

Bruchard, R.P., D. Rittschof, and J. Bonaventura. **1991.** Adhesion and motility of gliding bacteria substrata of different surface free energies. *Appl. Environ. Microbiol.* 56(8):2529:2534.

Rittschof, D., A.R. Schmidt, I.R. Hooper, D.J. Gerhart, D. Gunster, and J. Bonaventura. **1991.** Molecular mediation of settlement by selected invertebrate larvae. In: *Bioactive Compounds from Marine Organisms,* M.-F. Thompson, R. Sarojini, and R. Nagabhushanam (eds.), pp. 317-330. Oxford and IBH Publ. Co., New Delhi.

Roberts, D., D. Rittschof, E. Holm, and A.R. Schmidt. **1991.** Factors influencing larval settlement: Temporal, spatial and molecular components of initial colonization. *J. exp. Mar. Biol. Ecol.* 150(2):203-222.